

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-062082

(43)Date of publication of application : 07.03.1995

(51)Int.Cl.

C08G 65/18  
C08G 65/18

(21)Application number : 05-214834

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INST

(22)Date of filing : 09.08.1993

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## (54) ACTIVE-ENERGY-RAY-CURABLE COMPOSITION

### (57)Abstract:

PURPOSE: To provide an active-energy-ray-curable compsn. which comprises an oxetane-ring-contg. compd., an oxirane-ring-contg. compd., and a polymn. initiator, is excellent in adhesiveness and resistances to heat and chemicals, has a quick curability though having a low viscosity, and is useful for coatings, etc.

CONSTITUTION: This compsn. comprises an oxetane-ring-contg. compd. (A) [pref. a compd. of formula I (wherein R<sub>1</sub> is ethyl; R<sub>2</sub> is butyl or benzyl; and Z is O), or the like], an oxirane-ring-contg. compd. of formula II (B) (pref. bisphenol A polyglycidyl ether or the like), and a compd. (C) which initiates cationic polymn. on

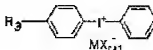
exposure to an active energy ray [pref. a compd. of formula III (wherein R<sub>3</sub> is H, 1-18C alkyl or the like; M is antimony; X is F; and n is 6), etc.]. Pref., the compsn. comprises 10-40 pts. ingredient A, 90-60 pts. ingredient B (the sum A and B being 100 pts.), and 0.1-10 pts. ingredient C.



I



II



III

\* NOTICES \*

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the activity energy-line hardening setup-of-tooling product which gives the hardened material which hardened promptly by the exposure of activity energy lines, such as ultraviolet rays or an electron beam, and was excellent in adhesion with a substrate.

[0002]

[Description of the Prior Art]In various industries, such as coating of the various characteristics, such as the quick cure rate, good workability by generally being a non-solvent, and a very low energy requirement, to wood, metal paint, and printing, activity energy-line hardening art is very important. In the early development in this field, research is concentrating on polyfunctional acrylate and the activity energy-line start radical polymerization of unsaturated polyester, and such materials are still used in large quantities even today. Also in the present, although most of these researches are turned to the activity energy-line start radical polymerization, optical start being also ionic polymerization and being also quite promising in many applicable fields are fully admitted. Since especially optical start cationic polymerization is rich in various possibilities of chemical and realizing a physical characteristic, by the polymerization of various monomers, it is attractive. Since a polymerization is not checked by oxygen, it is not necessary to carry out optical start cationic polymerization under an inert atmosphere, and it has the advantage that a prompt and perfect polymerization can be performed in the air. Optical start cationic polymerization art was concentrated on development of photopolymerization of two kinds of monomers called the epoxy resin and vinyl ether compound which have an oxirane ring which is 3 membered-ring cyclic ether till today. In particular, heat resistance is high, it excels in an adhesive property, and it is known for photopolymerization of an epoxy resin that coating with good chemical resistance will be

obtained. However, photo-curing speed is not enough for the conventional photoresist epoxy resin, and it has many which have still higher viscosity. Although the method of carrying out a viscosity down by blending a monofunctional epoxy compound as reactive diluent is also tried, if it is going to make viscosity less than into practical viscosity, i.e., 5000 cps, it has the problem that a cure rate falls further. For this reason, the conventional photo-curing type epoxy resin was not able to be used for the paper which needs prompt photo-curing, and a use like plastic coating. Therefore, the activity energy-line hardening setup-of-tooling product which has practical viscosity and maintains a cure rate had been desired, employing the characteristic of an epoxy resin efficiently. Polyfunctional epoxide to which the polyfunctional oxetane monomer which has an oxetane ring which is 4 membered-ring cyclic ether in a polymerization nature functional group in recent years is equivalent, and equivalent, or -- having a photoresist beyond it is reported (journal OBU macromolecular science .A -- 915 pages No. 10 29 volumes in 1992.) The photo-curing setup-of-tooling product which uses a polyfunctional oxetane monomer as the main ingredients is proposed as what has fast curability in said A30 volume, No. 2&3, 189 pages, and 1993 in said A30 volume, No. 2&3, 173 pages, and 1993 (Japanese Patent Application No. No. 49907 [ five to ]).

[0003]

[Problem(s) to be Solved by the Invention]The purpose of this invention is to provide the activity energy-line hardening setup-of-tooling product which solves the above-mentioned problem, which has good heat resistance, an adhesive property, and chemical resistance, and polymerizes by short-time optical exposure and in which hypoviscosity also has fast curability.

[0004]

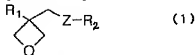
[Means for Solving the Problem]A compound which has one oxetane ring in a molecule as a result of this invention persons' inquiring wholeheartedly in view of such the actual condition, An activity energy-line hardening setup-of-tooling product which consists of a compound which has one or more oxirane rings in a molecule maintains good various characteristics, and also found out having quick hardenability and completed this invention. That is, this invention relates to an activity energy-line hardening setup-of-tooling product which consists of a compound which makes cationic polymerization start by the exposure of a compound 3 activity energy line which has one or more oxirane rings in compound 2 molecule which has one oxetane ring in 1 molecule. A constituent of this invention makes it the feature to have fast hardening also in hypoviscosity, maintaining the characteristic which an activity energy-line hardening setup-of-tooling product which used the conventional epoxy resin had that heat resistance is high, excel in an adhesive property, and coating with good chemical resistance is obtained. This invention is explained in detail below.

[0005]O In compound this invention which has one oxetane ring in a molecule, as a compound (henceforth compound A) which has one oxetane ring in a molecule, If it is a compound which

has one oxetane ring in a molecule, various things can be used, and as a desirable compound, a compound expressed with a following formula (1) can be mentioned.

[0006]

[Formula 1]



[0007] Here, in a formula (1), Z is oxygen or sulfur. R<sub>1</sub> is the alkyl group of 1-6 carbon numbers, such as a hydrogen atom, a fluorine atom, a methyl group, an ethyl group, a propyl group, or a butyl group, the fluoro alkyl group of 1-6 carbon numbers, an allyl group, an aryl group, a furil group, or a thienyl group. R<sub>2</sub> The alkyl group of 1-6 carbon numbers, such as a methyl group, an ethyl group, a propyl group, or a butyl group, 1-propenyl group, 2-propenyl group, a 2-methyl-1-propenyl group, The alkenyl group of 1-6 carbon numbers, such as a 2-methyl-2-propenyl group, 1-butenyl group, 2-butenyl group, or 3-butenyl group, Aryl groups, such as a phenyl group, benzyl, fluorobenzyl, a methoxybenzyl group, or a phenoxyethyl group, The alkyl carbonyl group of 1-6 carbon numbers, such as a propylcarbonyl group, a butyl carbonyl group, or a pentyl carbonyl group, The alkoxy carbonyl group of 1-6 carbon numbers, such as an ethoxycarbonyl group, a propylcarbonyl group, or a butyl carbonyl group, The alkoxy carbamoyl group of 1-6 carbon numbers, such as an ethoxycarbamoyl group, a propylcarbamoyl group, or a butylpentylcarbamoyl group, etc. are mentioned.

[0008] A thing of a low-grade alkyl group has preferred R<sub>1</sub>, and a thing of an ethyl group is [ in / at this invention / the above-mentioned formula (1) ] more preferred. R<sub>2</sub> are a butyl group and benzyl preferably. Z is oxygen preferably.

[0009] In this invention, two or more kinds of the above-mentioned compounds A can be used together.

[0010] O Compounds (henceforth the compound B) which have one or more oxirane rings in a molecule used into a molecule by compound this invention which has one or more oxirane rings are one or more oxirane rings in a molecule. [0011]

[Formula 2]



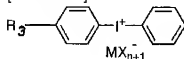
[0012] It is a compound which \*\*\*\*, and if used as an epoxy resin, it is usually usable in either a monomer oligomer or polymer. As an example of the compound B, publicly known aromatic epoxy resin, an alicycle follows epoxy resin, and an aliphatic series epoxy resin are mentioned conventionally. An epoxy resin means a monomer, oligomer, or polymer below. A thing

desirable as aromatic epoxy resin is JI or poly glycidyl ether manufactured by the reaction of the polyhydric phenol which has at least one aromatic core, or its alkylene oxide adduct and epichlorohydrin, For example, JI of JI of bisphenol A or its alkylene oxide adduct or poly glycidyl ether, hydrogenation bisphenol A, or its alkylene oxide adduct or poly glycidyl ether, novolak type epoxy resin, etc. are mentioned. Ethyleneoxide or propylene oxide is mentioned as alkylene oxide here. As an alicycle follows epoxy resin, the compound which has cycloalkane rings, such as KISEN or a cyclopentene ring, to at least one cyclo, Cyclohexene oxide or the cyclopentene oxide content compound obtained by epoxidating with suitable oxidizers, such as hydrogen peroxide and a peroxy acid, has it, and as an example, [ preferred ] 3, the 4-epoxycyclohexylmethyl 3, 4-epoxycyclohexylcarboxylate, etc. are mentioned. As a desirable thing of an aliphatic series epoxy resin, There is JI or poly glycidyl ether of aliphatic polyhydric alcohol or its alkylene oxide adduct, etc., and as the example of representation, Diglycidyl ether of ethylene glycol, diglycidyl ether of propylene glycol, or diglycidyl ether of alkylene glycol, such as diglycidyl ether of 1,6-hexanediol, Poly glycidyl ether of polyhydric alcohol, such as JI of glycerin or its alkylene oxide adduct, or triglycidyl ether, Diglycidyl ether of polyalkylene glycols, such as a polyethylene glycol or diglycidyl ether of the alkylene oxide adduct, a polypropylene glycol, or diglycidyl ether of the alkylene oxide adduct, etc. are mentioned. Ethyleneoxide or propylene oxide is mentioned as alkylene oxide here. Monoglycidyl ether of aliphatic higher alcohol which is a monomer which has one oxirane ring, phenol, cresol or monoglycidyl ether of such alkylene oxide adducts, etc. can be used for intramolecular other than these compounds. In this invention, two or more kinds of the above-mentioned compounds B can be used together.

[0013]O As a compound (henceforth the compound C) which makes cationic polymerization start by the exposure of a compound activity energy line which makes cationic polymerization start by the exposure of an activity energy line, publicly known various cationic photopolymerization initiators can be used conventionally. As a desirable thing, diaryliodonium salt and a triarylsulfonium salt are mentioned among these initiators. A typical photopolymerization initiator is shown below.

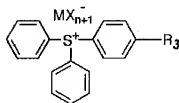
[0014]

[Formula 3]



[0015]

[Formula 4]



[0016] (R<sub>3</sub> is hydrogen, an alkyl group of various length of the carbon numbers 1-18, or an alkoxy group of the carbon numbers 1-18 among a formula -- M -- metal -- it is antimony preferably -- X -- halogen -- it is fluoride preferably, and n is a metaled valence, for example, in the case of antimony, it is 6)

[0017] O Inerts like an inorganic bulking agent, a color, paints, a viscosity modifier and a processing agent, and an ultraviolet-rays interception agent besides the above-mentioned essential ingredient can be blended with a constituent of other ingredient this inventions.

[0018] When stiffening a constituent of this invention by visible light, or when making it harden by ultraviolet rays, in addition to the compound C, a photosensitizer can also be blended in order to improve hardenability further. As for a typical sensitizer which can be used in this invention, Crivello is ADOBANSUDO. Yne It is possible to use a compound currently indicated by polymer science (Adv. in Plymer Sci., 62, 1 (1984)). As an example, there are pyrene, perylene, an acridine orange, a thioxan ton, 2-chloro thioxan ton, a PENZO flavin, etc.

[0019] O What is necessary is just to mix the above-mentioned compound A, and B and C in accordance with a conventional method as a manufacturing method of an activity energy-line hardening setup-of-tooling product of manufacturing method this invention. Here, as for compound A, it is preferred to carry out 5-50 weight-section combination to total quantity 100 weight section of compound A in a constituent and the compound B, and it is ten to 40 weight section more preferably. In fully being unable to hypoviscosity-ize a constituent when loadings of compound A are less than five weight sections, and exceeding 50 weight sections, there is a case where it becomes impossible to maintain fast curability. As for the compound C, it is preferred to blend 0.01-20 copies to total quantity 100 weight section of compound A and the compound B, and it is 0.1 to 10 weight section more preferably. In fully being unable to stiffen a constituent when loadings of the compound C are less than 0.01 weight sections, and exceeding 20 copies, there is a case where a light transmittance state becomes poor and uniform hardening becomes impossible. What is necessary is just to determine a compounding ratio of compound A and the compound B in consideration of viscosity of a constituent demanded, hardness of a hardened material, etc. in a mentioned range in practice.

[0020] O Harden easily a constituent of the fast curability of directions-for-use this invention by irradiating with activity energy lines, such as ultraviolet rays, X-rays, or an electron beam. When irradiating with ultraviolet rays, various light sources can be used, for example, it can be made to harden by mercury arc lamp, xenon arc lamp, fluorescent lamp, carbon arc lamp, a

tungsten halogen copy lamp, and irradiation light from the surrounding daylight. When irradiating with ultraviolet rays, irradiation intensity to a substrate is a 0.01 W square centimeter at least, and it is preferred to enable it to harden continuously with paper or a metallic coating line by hardening a constituent within 1 to 20 seconds. When making it harden with an electron beam, it is made to usually harden with an electron beam of the following 300-eV energies, but it is possible to also make it harden in an instant with a dose of 1Mrad - 5Mrad.

[0021]A constituent of this invention is applicable to substrates, such as metal, rubber, a plastic, forming parts, a film, paper, a tree, a woven glass fabric, concrete, and ceramics.

[0022]As a use of a constituent of this invention, protection, an ornament and coating for an insulation, a \*\*\*\* compound, printer's ink, sealant, adhesives, photoresist, a wire insulating material, textile coating, a lamination, an impregnated tape, a printing plate, etc. are mentioned, for example.

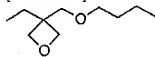
[0023]

[Example]An example and a comparative example are raised to below, and this invention is more concretely explained to it. The part in an example and a comparative example is a weight section as long as there is no notice especially.

[0024]As example 1 compound A to ten copies of following compounds (2), and the constituent which mixed 90 copies of bisphenol A diglycidyl ether as compounds B. Five copies of Adeka Optomer SP-170 (the Asahi Electrification company products, 50% of active principle) was added and mixed as the compound C, and the activity energy-line hardening setup-of-tooling product was prepared.

[0025]

[Formula 5]



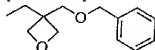
(2)

[0026]After applying the obtained constituent so that it may become about 20 microns to a steel plate, The number of passes until stickiness disappears from the surface was measured using the black light (lump height = 10-cm, conveyor speed =10 m/min, and irradiation intensity:  $310\text{mW/cm}^2$ ,  $76\text{mJ/cm}^2$ ) of the conveyor type which installed the high-pressure mercury-vapor lamp of 80 w/cm. (Let 10 m/min be an one pass) About the obtained hardened material, crosscut back tape exfoliation was carried out and adhesion was evaluated. Measurement of viscosity was measured at 25 \*\* using the Brookfield viscometer.

[0027]The compound (2) or the following compound (3) was used as Example 2 - 6 compounds A by the composition ratio which showed bisphenol A diglycidyl ether in Table 1 as the compound B, and the constituent was prepared like Example 1. It evaluated like [ constituent / which was obtained ] Example 1. The result is shown in Table 1.

[0028]

[Formula 6]



(3)

[0029]

[Table 1]

実施例	化合物 A〔部〕	化合物 B〔部〕	硬化性 <sup>1)</sup>	粘度 <sup>2)</sup>	密着性
1	化合物 (2) 〔10〕	ビスフェノール A〔90〕 ジグリシジルエーテル	3	1500	○
2	同上〔20〕	同上〔80〕	4	130	○
3	同上〔30〕	同上〔70〕	4	30	○
4	化合物 (3) 〔10〕	同上〔90〕	3	3000	○
5	同上〔20〕	同上〔80〕	4	400	○
6	同上〔30〕	同上〔70〕	5	85	○

1) 単位はパス

2) 単位は c p s

[0030] It evaluated like Example 1 except having used the compound B, as shown in the one to comparative example 3 table 2. The result is shown in Table 2.

[0031]

[Table 2]



比較例	化合物 B (部)		硬化性 <sup>1)</sup>	粘度 <sup>2)</sup>	密着性
1	ビスフェノール A (100) ジグリシジルエーテル	0	3	14000	○
2	同上 (90)	フェニルグリシジ (10) ルエーテル	4	2200	○
3	同上 (80)	同上 (20)	6	260	○
4	同上 (70)	同上 (30)	9	55	○

1) 単位はパス

2) 単位は c p s

[0032]

[Effect of the Invention] Since it is cured fast by the activity energy-line exposure of ultraviolet rays or an electron beam even if the activity energy-line hardening setup-of-tooling product of this invention is hypoviscosity, and it excels in adhesion with a substrate, The influence which can be used for various uses, such as protection, an ornament and coating for an insulation, a \*\*\*\* compound, printer's ink, sealant, adhesives, photoresist, a wire insulating material, textile coating, a lamination, an impregnated tape, and a printing plate, and it has on the industrial world is size.

[Translation done.]